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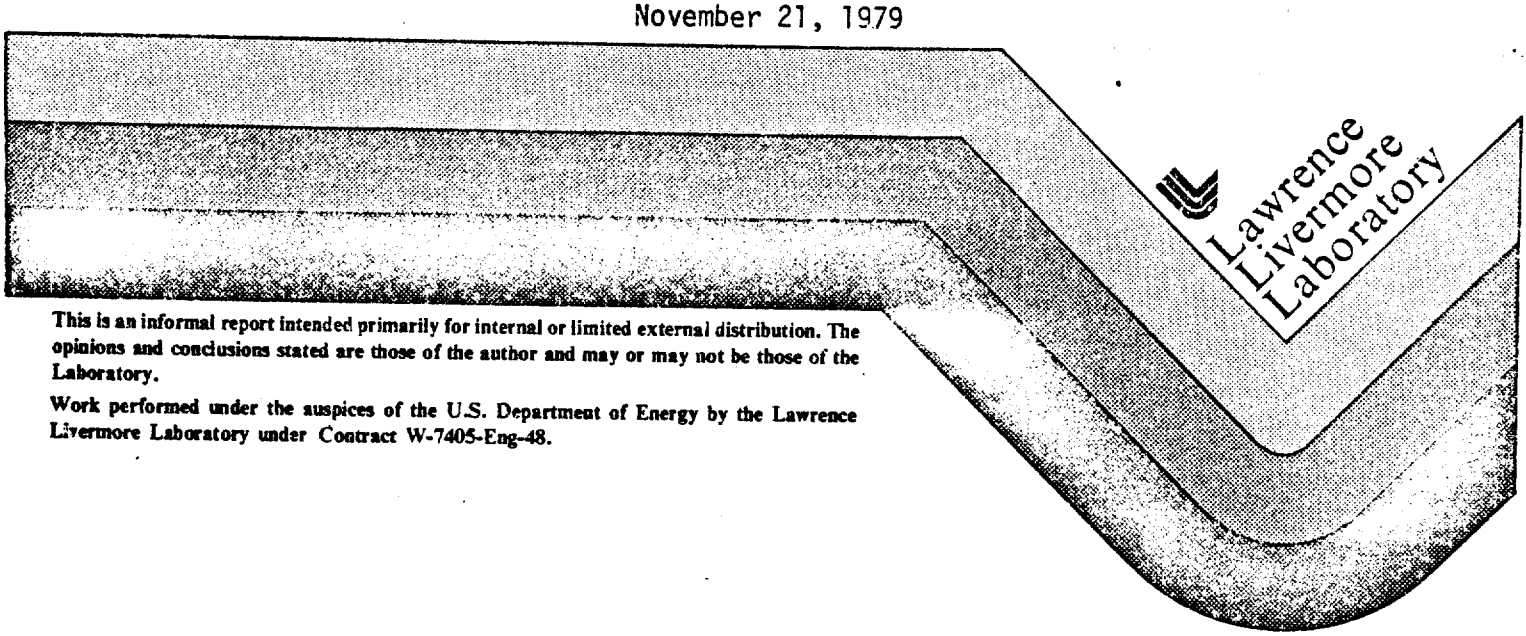
EMISSIONS FROM ADVANCED FOSSIL-FUEL COMBUSTION TECHNOLOGIES

Summary of Project Status

J. M. Ondov

November 21, 1979



Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

EMISSIONS FROM ADVANCED FOSSIL-FUEL COMBUSTION TECHNOLOGIES

Summary of Project Status

J.M. Ondov

Terrestrial and Atmospheric Sciences

Lawrence Livermore Laboratory

I. Current Field Experiments and Work in Progress; Calendar Year 1979

II. Activities planned for FY 1980, Jan. - Oct.

III. In-house Collaboration

IV. Publications and Papers Presented, Calendar Year 1979.

V. Personnel and Distribution of Funds.

Summary of On-going and Planned Activities

I. Current field experiments and work in progress, calendar year 1979.

A. San Juan Power Plant, March 1979.

- Tests of impaction and filtration substrates.
- Tests of vapor-sampling techniques.

B. Huntington Canyon Power Plant, July 25-27.

- Stack aerosol particle and gas collection at ambient temperature.

C. Hunter Power Plant, July 25 - August 6.

- Determination of removal efficiency and effects of venturi-spray tower, flue-gas desulfurization system on aerosol particles, inorganic and organic vapors.
- Characterization of vapor vs particulate fractionation of volatile inorganic species, eg. As, Se.

D. Huntington/Hunter Power Plants:

- Studies of mechanisms of the formation and chemical enrichment of aerosol particles by analyzing size-segregated fly-ash particles in the size range 0.05 to $\geq$ 30μm, collected by low pressure impaction.

E. Four Corners/San Juan/Hunter

- Studies of surface area and morphology (especially particle porosity and carbon content) for correlation with vapor vs particle residence and surface-layer depth of chemical constituents, and chemical enrichments of aerosol particles.
- Identification of Se compounds in fly ash from electrostatic precipators - to permit comparison of control devices for removal of Se.

II. Work planned for calendar year 1980

- Characterization of aerosol and vapor emissions from:
  - NEPSCO's 80-MW(e) Unit No. 1 fired with coal-oil mixtures.
  - 30-MW(e) Fluidized Bed Combuster, Rivesville, West Va.
  - Davies power-gas, Welman-Lord Flue-gas desulfurization system at the San Juan power plant (planned as a back-up to the above).

- Development of techniques to identify and quantitate levels of trace organo-sulfur compounds.

- Procurement of ultra-high-volume (175 cfm) isokinetic air sampling system.

- Continuation of surface-area, and low-pressure-impactor (ie., fine particle) studies, and continuation of chemical speciation studies of Se and other elements.

III. In house collaborative projects

- Fate of organic compounds from coal combustion in effluents from particulate scrubbers and flue-gas desulfurization systems; with Dr. Florence Harrison and George Cameron.

- Mutagenicity of coal fly ash in mammalian cell systems (i.e., Chinese hamster ovary cells); with Dr. Robert Taylor.

- Development of a sophisticated computer code simulating atmospheric interactions including sedimentation and coagulation by Mrs. Helen Buckholtz, a graduate student at the Davis - Livermore Applied Science Center in collaboration with Dr. Arthur Biermann is nearly complete. The code can handle multimodal aerosol-particle distributions, and is applicable to particle emissions from point-source combustion technologies.

IV. Publications (calendar year 1979):

A.H. Biermann, J.M. Ondov, Application of Surface-Deposition Models to Size-Fractionated Coal Fly Ash. Atmos. Environ. (In press).

J.M. Ondov, R.C. Ragaini, A.H. Biermann, Emissions and Particle Size Distributions of Minor and Trace Elements at Two Western Coal-Fired Power Plants Equipped with Cold-Side Electrostatic Precipitators. Environ. Sci. Technol. 13 946-953 (1979).

J.M. Ondov, R.C. Ragaini, A.H. Biremann, Elemental Emissions from a Coal-Fired Power Plant. Comparison of a Venturi Wet Scrubber System with a Cold-Side Electrostatic Precipitator. Environ. Sci. Technol. 13 598-607 (1979).

D.G. Coles, R.C. Ragaini, J. M. Ondov, G.L. Fisher, D. Silberman, B.A. Prentice, Chemical Studies of Stack Fly Ash from a Coal-Fired Power Plant. Environ. Sci. Technol. 13 455-459 (1979).

G.L. Fisher, D. Silberman, B.A. Prentice, R.E. Heft, J.M. Ondov, Filtration Studies with Neutron-Activated Coal Fly Ash. Environ. Sci. Technol. 13 689-693 (1979).

IV. Papers Presented (calendar year 1979)

A.H. Biermann, J.M. Ondov, Application of Surface-Deposition Models to Size-Fractionated Coal Fly Ash. American Chemical Society/Chemical Society of Japan, Chemical Congress, Honolulu, April 1-6 (1979).

J.M. Ondov, A.H. Biermann, Physical and Chemical Characterization of Aerosol Emissions From Coal-Fired Power Plants. Invited Paper, Symposium on Environmental and Climatic Impact of Coal Utilization, Williamsburg, April 17-19 (1979).

J.M. Ondov, A.H. Biermann, Effects of Particulate Control Devices on Atmospheric Emissions of Minor and Trace Elements From Coal Combustion. Invited Paper, 2nd Symposium on the Transfer and Utilization of Particulate Control Technology, Denver, July 23-24 (1979).

V. Distribution of Personnel and Funding

	Funding $309,000	FTE FY80	FTE FY79
J.M. Ondov Aerosol Chemist	Project Management Analytical Support Field Support Data Reduction	0.7	1.0
A.H. Biermann Aerosol Physicist	Particle Sizing Surface Areas Electron Microscopy X-ray Microprobe Field Support Data Reduction	0.6	1.0
M.A. Tompkins Analytical Chemist	Trace Organic Analyses Gas Chromatography; High Performance Liquid Chromatography	0.2	0.7
C. Morris Analytical Chemist	Gas Chromatography - Mass Spectrometry	0.1	0.0
R.E. Heft Physical Chemist	Inorganic Analyses Instrumental Neutron Activation, Atomic absorbtion, x-ray fluoresence	0.2	0.3
R. Kozykowski Chemical Technic.	Sample prep for inorganic analyses	0.5	
V. Housinkfeld Chemical Technic.	Sample Prep Organic Anal., Se Speciation Study -Ion Chromatography Ames Testing	0.4	
J. McNabb	Maintenance of field sampling equipment Field Support		
D. Garvis Mechanical Technic.	Field Support Service field equipment		
	To		

Field Sampling Budget

Summary of on-going work

A. San Juan Power Plant, Farmington, New Mexico.

1. A final report on the first set of experiments conducted at the stack-sampling location, downstream from the hot-side electrostatic precipitators (ESPs) at San Juan is nearly completed and will be submitted for publication in Environmental Science and Technology. The paper contains results of the most recent experiments conducted at San Juan before the scrubber systems were installed. Conclusions based on comparisons of relative concentrations of minor and trace elements in total suspended aerosol particles and in discrete size fractions are as follows:

   - The hot-side ESP may less effectively collect Se, Mo, Cr, and to a lesser extent As, Ba, Ga, U, V, and In, than the cold-side ESP units that we tested.

   - Mass balances and limited vapor determinations of trace elements indicate that, except for Hg, Se, and Cl, the amounts of the elements emitted as vapor are quite small relative to the total quantities in coal, but may be large compared to the quantities emitted on particles.

   - The quantities of Se, Cd, As, Mo, and Sb emitted as vapor at three coal-fired power plants were also small relative to the vapor pressures predicted for their volatile oxides or metal forms.

2. During a 2-day field trip in March, 1979, aerosol-particulate, inorganic vapor, and organic vapor samples were collected downstream from the air preheater and hot-side ESP. The purpose of the sampling was to test alternative impaction and filtration substrates and to test the vapor-sampling systems. The number of successful experiments was limited because of a unit outage during about 30% of the available sampling time. Analyses of these samples are now complete.

   - Filter substrate tests show that the particulate collection efficiency of quartz fiber, Teflon, and Teflon filters with nylon backing were all adequate (i.e., >93% as determined by comparing total aerosol mass or mass of individual elements on tandem filter pairs: see Table 1 of the Appendix). Of greater concern was the possibility that either the filter or impactor substrates or particles collected on the substrates could adsorb Se or other elements in the vapor phase, thereby increasing the amount of the element attributed to the particulate phase. As shown below, the concentration ratio Se:Sc was about 35% larger in the 45-min particulate sample collected on a Fluoropore (i.e., nylon-backed Teflon) filter than in the 6-min sampled collected on a similar Mitex

(Teflon with no backing) filter. The ratios of Ga and In (to Sc) were about 50% larger in the 45-min. sample and that of As was about 80% larger. The ratios of most of the elements to Sc in the two samples agreed within the uncertainties, but are uniformly larger in the 45-min. sample. The differences in the ratios of Group 1 elements to Sc (e.g., the elements whose concentrations are enriched relative to their concentrations in coal) tend to be larger (see Table 1). This may suggest that the measured concentration depends on sampling time. Such would be the case if the efficiency of collection of fine particle components increased with time or if additional vapor-phase components were deposited at some rate. No such differences were observed in seven, consecutive aerosol samples collected in an earlier experiment with Fluoropore filters at the stack-sampling location, when sampling times ranged from 13 to 29 min.

Table 1. Ratios of elements in aerosol particles collected on Mitex and Fluoropore filters at the San Juan Power Plant in March 1979.[a]

Group 1 (elements)	Mitex	Fluoropore	Group 2 (elements)	Mitex	Fluoropore
Se:Sc	23 ± 2	31 ± 1	Ce:Sc	6.1 ± 0.9	6.7 ± 0.7
Sb:Sc	0.67 ± 0.17	0.89 ± 0.08	Th:Sc	1.5 ± 0.2	1.6 ± 0.1
U:Sc	1.0 ± 0.15	1.3 ± 0.1	Sm:Sc	0.52 ± 0.03	0.63 ± 0.02
W:Sc	0.83 ± 0.38	1.2 ± 0.2	Fe:Sc	210 ± 190	2.70 ± 0.97
As:Sc	2.5 ± 0.2	4.5 ± 0.1			
Ga:Sc	6.7 ± 1.2	10 ± 0.5			
In:Sc	0.030 ± 0.008	0.046 ± 0.002			

[a] Sampling times, stack-gas temperatures, and total aerosol-mass loadings for the Mitex and Fluoropore samples were 6.0 and 45 min., 139 and 138°C, and 5.4 and ~5 mg/m^3, respectively.

Moreover, instrumental neutron activation analyses (INAA) of an impactor sample collected at a location just beyond the ESP/air preheater show decreasing Se-to-Al ratios in particles of decreasing size (see Fig. 1) The Se-to-Al ratios were fairly uniform throughout all particle sizes in aerosols previously collected at the stack-sampling location. We hypothesize that more of the Se was in the gas phase at the exit of the air preheater than at the stack-sampling location, thereby leaving particles at the former location depleted of Se. The transit time for gas between the locations is about 6 sec., and a 2 or 3° C drop in temperature generally occurs in transit.

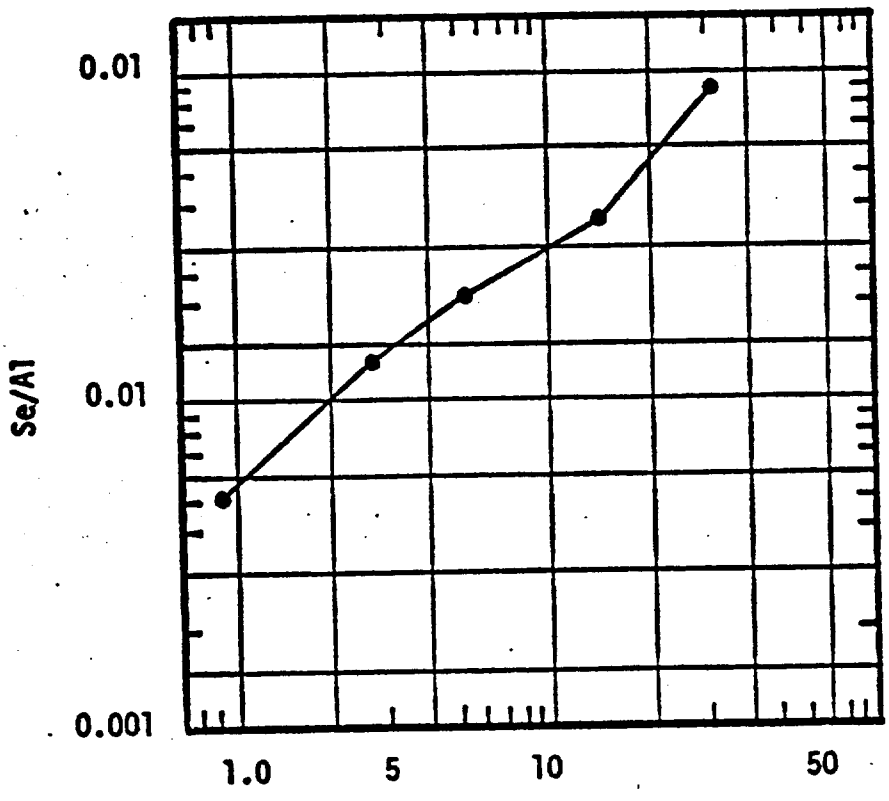


Figure 1. Ratio of Se and Aℓ Concentrations vs Particle Size in Fly Ash Collected at the ESP Outlet Location at the San Juan Power Plant.

- Inorganic vapors were collected by a glass-lined sampling system on precleaned charcoal supported in glass tubes. In this system, combustion gases are filtered in situ, i.e., the filter is located in the combustion-gas stream and operated at the prevailing temperatures (185 or 139° C), then diluted to cool the vapor and to prevent condensation of corrosive acid mists. Two samples were successfully collected; one collection lasting for 73 min. and run at 1:1 dilution with purified, dry nitrogen and the other lasting for 54 min. and run without dilution. The volumes of combustion gas collected were 0.16 and 0.26 (standard) m^3 for the diluted and undiluted samples, respectively. The concentrations of elements detected above blank by INAA are given in Table 2.

Table 2. Vapor concentrations of elements in combustion gas from the San Juan Power Plant, $\mu g/m^3$.

Element	Sample 1 (185°C)	Sample 2 (139°C)	Concentration predicted from mass balance
Se	8.1 ± 1.7	16 ± 1	~34
Sb	6 ± 2[a]	3	~4
W	6[b]	1.9 ± 0.2	~2
Cl	26,000 ± 4000	25,000 ± 2000	≤8600
As	6 ± 3	3	~0
Br	70 ± 30[a]	40	<12
Cr	360 ± 40	--	35
Mo	10	--	≥16
U	2	--	~2

[a] Successive sections of the trap contained comparable quantities.

[b] Value not considered reliable.

At flue-gas temperatures, trace elements may be volatile in the elemental form (i.e., Hg, Se, Cl, and Br), as oxides, chlorides, carbonyls, or perhaps in organometallic forms.

Selenium in particular is thought to occur in flue gases in the elemental state and, on the basis of vapor pressure data, is expected to occur totally in the gas phase at the temperatures at which both samples were collected. The Se concentrations measured in this experiment (8 and 16 $\mu g/m^3$) are much lower than one would predict, i.e., ~100 $\mu g/m^3$, on the basis of the Se content of the coal. The data suggest, therefore, that appreciable quantities of Se occur in nonvolatile forms, e.g., oxy anions, or that the vapor pressure of Se is reduced by adsorption phenomenon.

In general, the data listed above agree well with the concentrations in the vapor that are predicted from mass balance, considering the rather large uncertainties in the latter. We regard these data as only preliminary as more numerous and larger samples are required to assess the vapor components accurately. These data support our previous study (discussed above) at the San Juan plant.

B. Huntington Power Plant

Sampling was conducted on July 25-27 at Utah Power and Light's (UPL) Huntington Plant at sampling ports at the inlet to the cold-side ESP. The purpose of this work was to collect a highly resolved, size-fractionated aerosol-particle sample with our 11-stage impactor operated at low pressure and to collect samples of aerosol particles cooled to ambient temperature. The latter system was designed to permit equilibration of aerosol particles at ambient temperatures to facilitate mass transfer from gas to particles before aerosol-particle collection. Collected in this manner, the particulate samples may be expected to be more highly concentrated with respect to trace organic and inorganic species and thus possibly will reduce the sample size now required for chemical and biological analyses. If the gas-to-particle transfer proved to be quantitative (or at least accurately simulated processes occurring subsequent to atmospheric discharge), a further benefit could be the elimination of the difficult and time-consuming vapor-sampling techniques. The inlet sampling location was chosen for these experiments to minimize the sampling times.

The Huntington Plant consists of two identical 425 MW(e) coal-fired units equipped with cold-side ESPs and venturi spray-tower scrubbers. Scrubber operational problems precluded measurement of scrubbed combustion gases. This work was done at the UPL's Hunter Power Plant located about 20 mi. from the Huntington Plant.

1. Two low pressure impactor samples were collected at the Hunter Plant, respectively operated at minimum absolute pressures of 300 and 415 mm Hg. Both samples were collected with 47-mm Fluoropore back-up filters in a tandem holder. Two total aerosol samples were also collected on 62-mm fluoropore filters to compare with the impactor data.

   Small portions of each of the impactor substrates (Kapton film coated with Apiezon vacuum grease) were removed for analysis by scanning electron microscopy (SEM) and for particle sizing, The remaining portion of each substrate was submitted for neutron activation analysis.

   In Fig. 2, the vanadium mass per natural log size interval (dashed) curve, solid circles) and the relative concentration (i.e., ratio to Al) of vanadium (solid curve, open circles) are plotted against 50% cut-off diameters, estimated from nomographs provided by the designers of the impactor. Vanadium and Al were analyzed by INAA. These preliminary results suggest that the relative concentration of V in aerosol particles of diameters less than

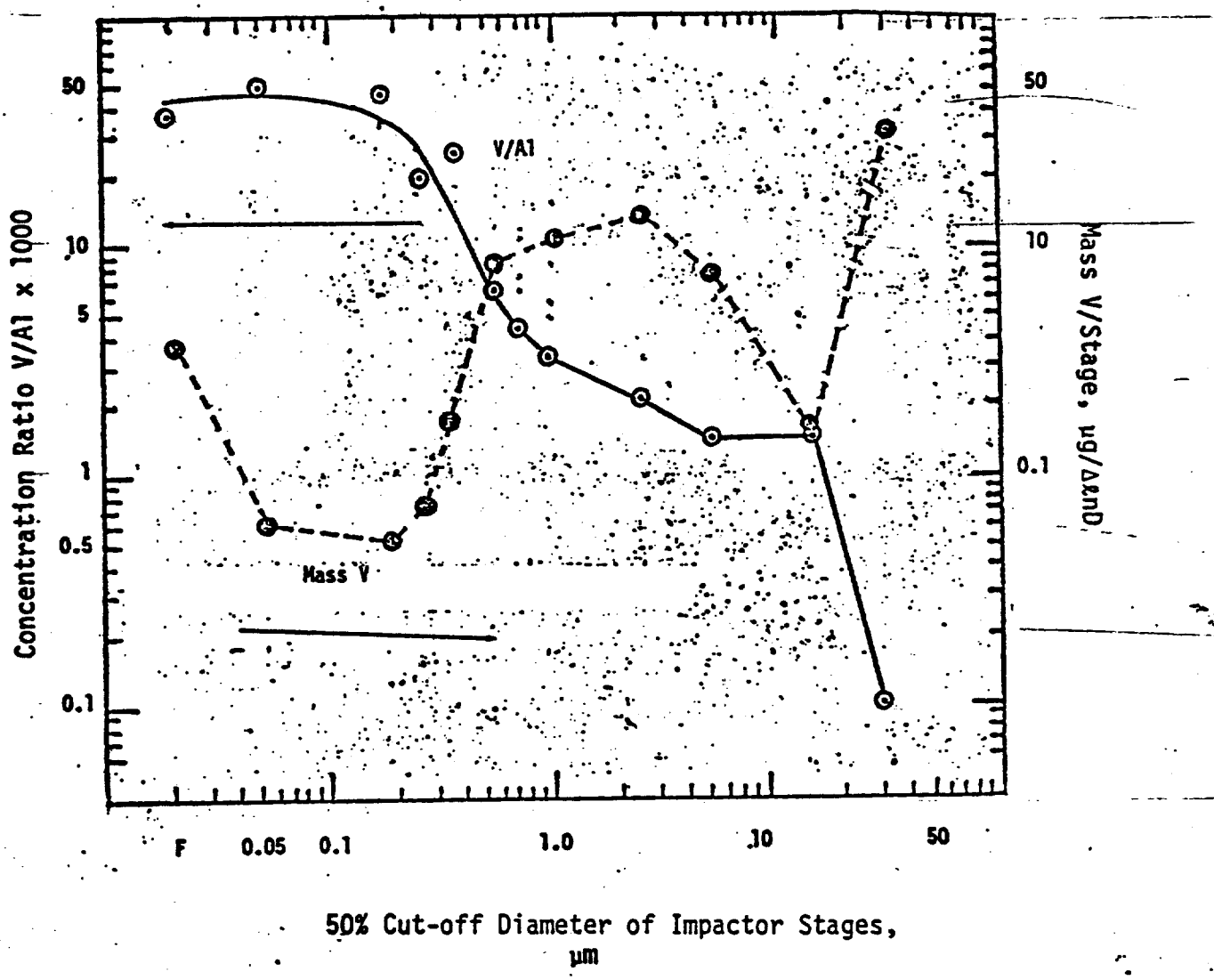


Figure 2. Distribution of mass and relative concentrations of Vanadium vs. impactor 50% cut-off diameters estimated from theoretical nomographs.

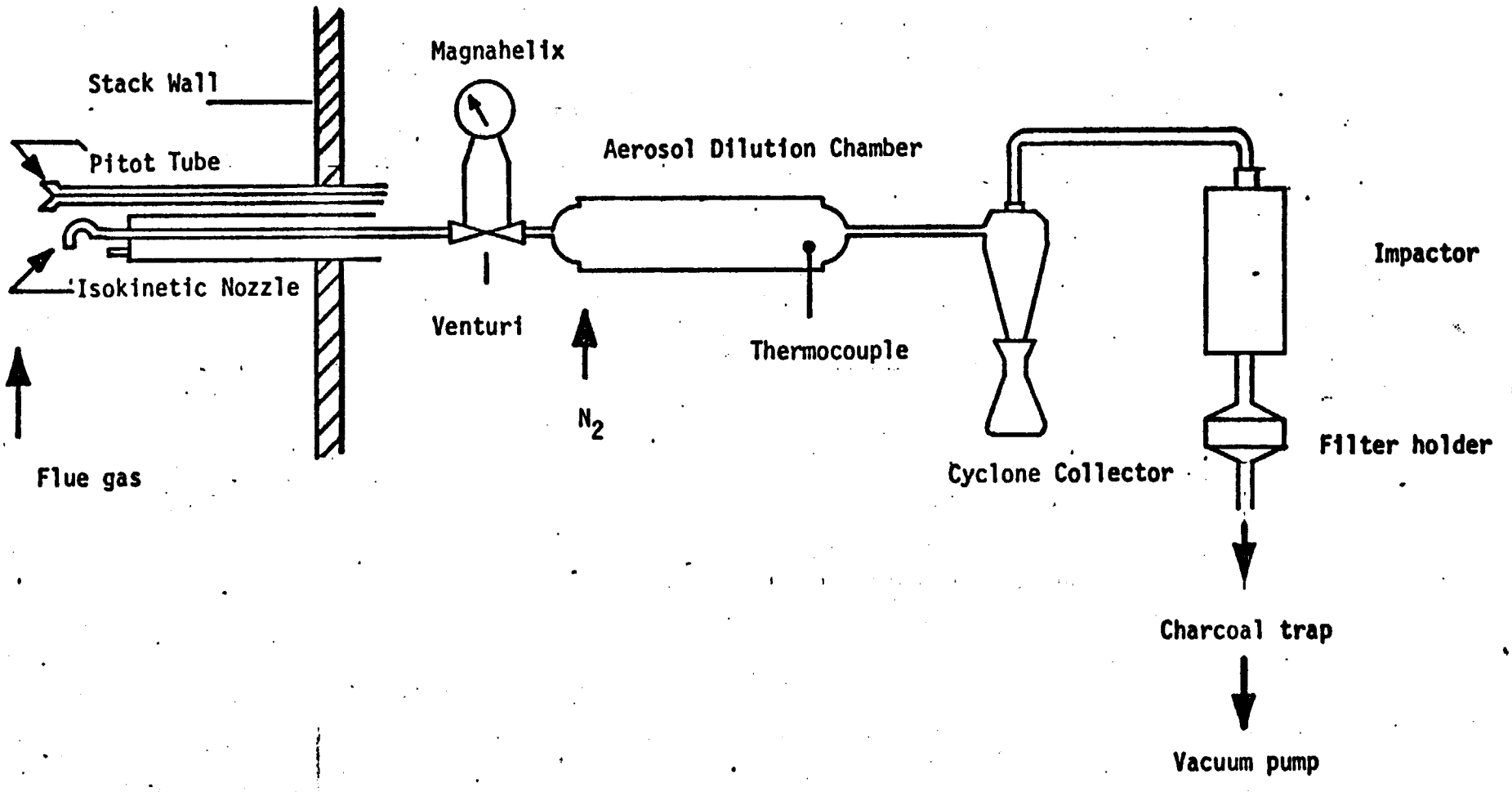
~0.2 μm are nearly uniform. This finding agrees well with our previous work (in press, see publications) in which we analyzed size-segregated fly-ash fractions of diameters ≥ 0.1 μm from another western coal-fired power plant. Significant adjustment of the size parameters is anticipated on the basis of preliminary SEM data, especially in larger particle fractions. A thorough analysis of the data must await SEM particle-sizing data and additional activation analyses. Further interpretation of the data will be facilitated by comparisons with fits to current vapor-deposition/chemical-enrichment models and with simulations of mass transport from aerosol coagulation.

2. Six aerosol-particulate samples were collected on precleaned, 62 mm quartz-fiber filters prceeded by a Pyrex cyclone separator and an aerosol dilution chamber. Aerosol particles were aspirated from the duct through a heated, Teflon-lined probe fitted with a "goose-neck" isokinetic sampling nozzle. The system is shown schematically in Fig. 3. The samples were collected after dilution with high purity nitrogen off-gas supplied from a liquid nitrogen Dewar flask at mixed gas temperatures of 31 to 35° C and dilution gas ratios of 2:1. Filter and impactor sampling times were kept to a maximum of 30 min. and 60 min., respectively, to minimize the potential for reactions with flue-gas components such as SO_x and NO_x. Three additional samplings were made in which a four-stage cascade impactor was installed between the cyclone preseparator and filter housing and two particulate samples were collected isokineticly at stack temperature for comparison. After collection the samples were immediately transferred to glass vials, purged with high purity N_2 and stored at dry ice temperature.

   A total of about 5 g of fly ash was collected with the dilution system, 1.4 g of which was collected downstream from the precyclone. A 90-mg aliquot of the fine fraction was extracted for 16 h with an azeotropic mixture of toluene and methanol and dried. The residue was dissolved in dimethyl sulfoxide and tested for mutagenicity in the Ames system with TA1538 bacteria with and without S9 activation. These results indicate no statistically signficant mutagenic response. Extraction of a 1-g portion of the fly ash fraction No. 3, for which mutagenic activity was reported by Christ et al., gave positive results (i.e., 162 revertants/mg normalized to 10^8 TA1538 bacteria). Preliminary SEM data indicate that the distribution of particles in our fine fraction is comparable to the mutagenic fly-ash fraction No. 3.

   Thus if the level of mutagens in fly-ash fraction No. 3 is typical of fly ash from utility pulverized coal combustion and mutagens do indeed become associated with particles at temperatures ≤ 90° C, then we would have been able to see significant mutagenic activity in a 90-mg sample. We are testing a larger, composite sample. The absence of significant mutagenic activity suggests that much larger samples are still required both for more detailed chemical analyses and for the Ames testing.

Figure 3. System for sampling aerosols at ambient temperature.



Aliquots of the combined samples are being analyzed for trace elements via INAA, and graphite-furnace atomic absorption spectroscopy. Profiles of trace organic compounds are being determined by fluorimetry, gas chromatography, and gas chromatography-mass-spectrometry.

C. Hunter Power Plant, Castle Dale, Utah

Extensive aerosol-particle and vapor samplings were performed at UP&L's Hunter Power Plant during the period July 27 to August 2. The Hunter Plant is nearly identical to the Huntington Plant. Aerosol and vapor samples listed in Tables 5-8 of the Appendix were collected concurrently at ports at the outlet of the cold-side ESP and in-stack, downstream from the lime-slurry scrubbing systems. The scrubbing system (see literature in the Appendix) consists of four vertical spray towers, each preceeded by a venturi separator. Each of the spray towers is connected to a common inlet and outlet manifold. During normal operation, three of the four towers are in service; the fourth tower is brought on line while one of the other units is serviced. Typically about 85% to 90% of the combustion-gas flow is scrubbed, the remaining portions are fed directly to the stack. Flue-gas levels of SO_2 were continuously monitored by UP&L at the ESP outlet, scrubber-inlet manifold, scrubber-outlet manifold, and in-stack at the same level as the particulate sampling ports.

In addition to samples of aerosol particles (i.e., collected on filters, and in cascade impactors), inorganic and organic vapors (see Table 2, Appendix), pulverized coal, bottom ash, ESP fly ash, and input and effluent streams were sampled from each of the operating spray towers as applicable. Table 11 of the appendix is a complete list of the bulk samples that were collected. Data on essential operational parameters, e.g., coal feed rate, electrical power output, pH of scrubber slurries, percent solids content (determined daily by plant personnel), and flue-gas composition were collected either hourly or as available.

1. Analyses in progress are as follows:

   - Minor and trace elements in total aerosol and size-segregated particulate samples via instrumental neutron activation analysis (INAA) and atomic absorption spectroscopy (AAS).
   - Particle morphology and individual particle composition via scanning electron microscopy (SEM) and x-ray microprobe spectroscopy (XRMS).
   - Particle sizing from SEM photographs of filtered and impacted particles.
   - Aqueous extractable anions via ion chromatography.
   - Volatile elements in charcoal vapor traps by INAA.
   - Trace organic compounds in XAD-2 resin traps by fluorometry, gas chromatography-mass spectrometry.

2. Results to date:

- Total aerosol particle mass determined by weighing filter samples collected at the ESP outlet and stack-sampling locations at the Hunter Plant are tabulated in Table 3. Successively determined stack aerosol-mass concentrations, measured downstream from the scrubber systems, were reproducible to within about 10% during a given period. These, in fact, never varied by more than 50% despite a range of a factor of six in the mass concentration of aerosol particles entering the scrubber systems as measured at the ESP outlet. The efficiency of aerosol-mass removal ranged from about 2 to about 89%, after correction for the quantity of gas bypassing the scrubber system. Our previous work with venturi scrubber systems showed that scrubbers actually generate particles, probably because of flash volatilization and mist entrainment mechanisms. The value of about 10 mg/m^3 may be the background level of the scrubber system, resulting from particle generation and may thus represent the minimum level of atmospheric emissions attainable when such systems are used.

- Ion-chromatography analyses. Portions of four filter samples were extracted at room temperature with a solution containing 0.003 M $NaHCO_3$ and 0.0023 M Na_2CO_3 and analyzed for soluble $SO_4^=$, $PO_4^=$, F^-, and Cl^- by ion chromatography. Two of the samples were collected at the ESP outlet and two in-stack. The data from filter samples are reported in Table 4. Samples of size-fractionated fly ash collected in eight-stage impactors operated at the ESP outlet and stack sampling locations were also analyzed by ion chromatography. To prevent interference in the analyses, the impaction substrates were not coated with adhesive materials. Because this was likely to affect the size distributions of particles collected on the individual stages, about 10% of each substrate was removed for particle sizing. Distribution parameters for aerosol particles collected on stages of the stack impactor are listed in Table 5. Concentrations of extractable Sulfate, Fluoride, Phosphate, and Chloride in the total aerosol (i.e., filter) samples are tabulated below. The concentrations of soluble $SO_4^=$ and F^- in particulate material (Table 4) are both enhanced by the scrubber system by factors of 2 to 4, and F^- by factors of 5 to 20. Soluble $PO_4^=$ and Cl^- show no clear trend.

  Concentrations of extractable sulfur in size-segregated particulate fractions sampled at locations in front of and beyond the scrubber system are shown in Figs. 4a and b. Figure 4b shows that sulfur is added in all of the particles and especially in those with 0.5- to 2-μm diameters.

D. Four Corners/San Juan/Hunter

1. Selenium Speciation. Selenium in the elemental state is insoluble in water, but will dissolve in concentrated H_2SO_4. Selenium dioxide, selanate, and selanites, however, are soluble in water

Table 3. Filter Samples from the Hunter Plant: Scrubber Efficiency Data.

DATE	LOCATION	FILTER #	AMT. OF COMBUSTION GAS BY-PASSING SCRUBBERS, %	AEROSOL MASS (mg/m^3)	PARTICULATE REMOVAL EFFICIENCY (%)	SO_2 REMOVAL EFFICIENCY (%)
7/28	Stack	LFP11	11.9	13.7	89	85
	ESP out	LFP25	11.9	62.7		85
	Stack	LFP21	11.6	15.1	86	85
7/29	Stack	LFP23	11.9	10.3	64	84
	ESP out	LFP33	10.3	23.8	63	84
	Stack	LFP24	10.75	8.8	71	83
	Stack	LNF42	10.8	9.8	66	85
	ESP out	LFP37	13.1	26.8	70-75	
7/31	Stack	LPF58	12.75	11.1		82
	ESP out	LFP57	13.13	16.7	38	83
	ESP out	LNF55	12.30	15.7	34	82
	Stack	LFP35	13.37	11.3	30	85
	Stack	LNF49	14.0	12.3	23	85
	ESP out	LFP64	13.43	15.3		85
8/01	Stack	LNF60	~ 16.9	10.0	7.9	~ 83
	Stack	LPF65		10.5		
	ESP out	LNF56	15.2	9.7 - 10.7	2.2	83

Table 4. Ion-chromatography Analyses of Filter Samples Collected at the Hunter Plant.

Location	Filter Material	$SO_4^{=}$		F^-		$PO_4^{=}$		Cl^-	
		µg/g	µg/m^3	µg/g	µg/m^3	µg/g	µg/m^3	µg/g	µg/m^3
Stack	Fluoropore	96500	1090	19500	220	2500	28	4400	49
ESP Outlet	Fluoropore	23000	350	3700	57	1450	22	-	-
Stack	Nuclepore	73000	900	18600	230	4200	52	1250	15
ESP Outlet	Nuclepore	34000	540	900	14	6900	110	9800	150

Table 5. Particle-size distribution parameters based on scanning electron micrographs. Particles were collected on stages of the stack impactor on uncoated polycarbonate substrates.

MK3-3 Impactor Stage	N[a]	σg	M_{50}[b]	σg	MMAD[c]
1	2.87	1.36	4.13	1.44	6.1
2	4.44	1.47	6.04	1.30	9.5
3	1.77	1.57	2.91	1.46	4.3
4	1.13	1.38	1.74	1.62	2.6
5	0.69	1.29	0.85	1.32	1.3
6	0.53	1.41	1.06	1.89	1.6
7	0.22	1.47	0.40	1.55	0.59

a Number median diameter and geometric standard deviation of log normal fits of the distributions.

b Mass medians from mass probability vs particle diameter plots constructed from transformed number distributions.

c Estimated mass median aerodynamic diameters, assuming uniform density of 2.2 g/cc.

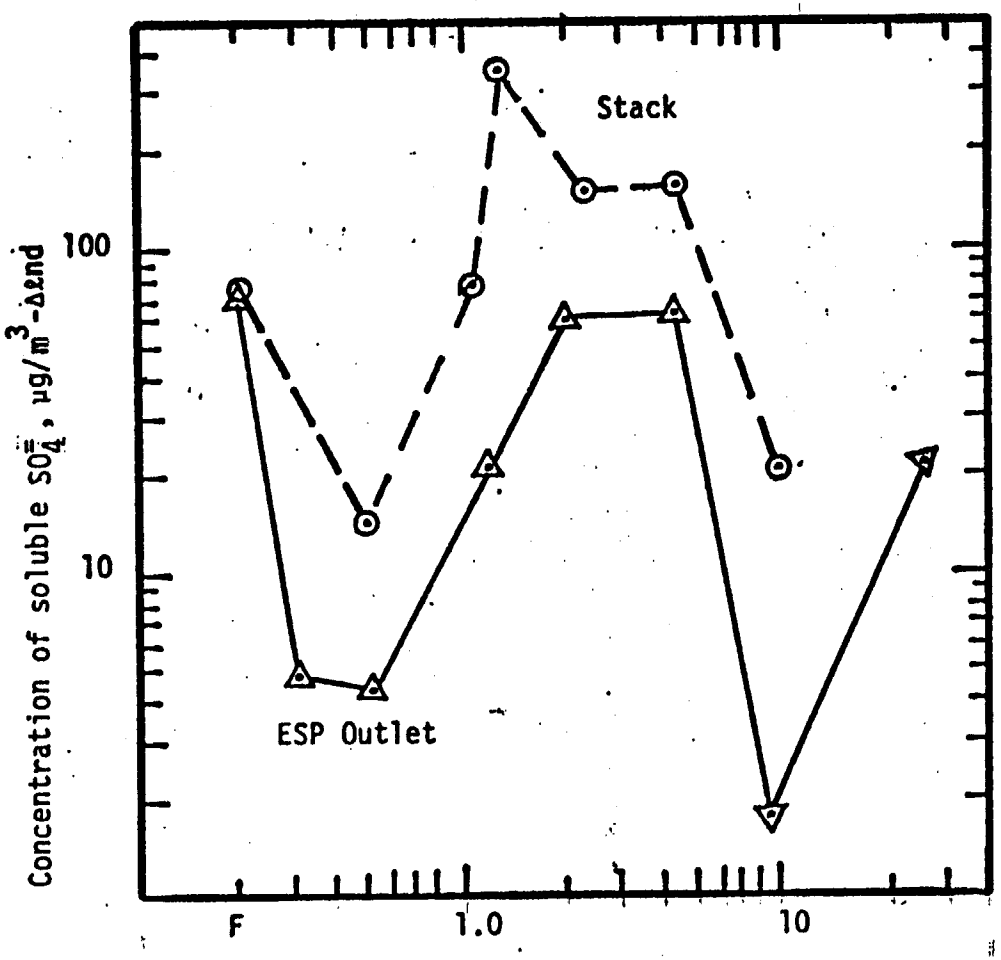


Figure 4a. Concentrations of soluble $SO_4^=$ on aerosol particles are enriched by a flue gas desulfurization system.

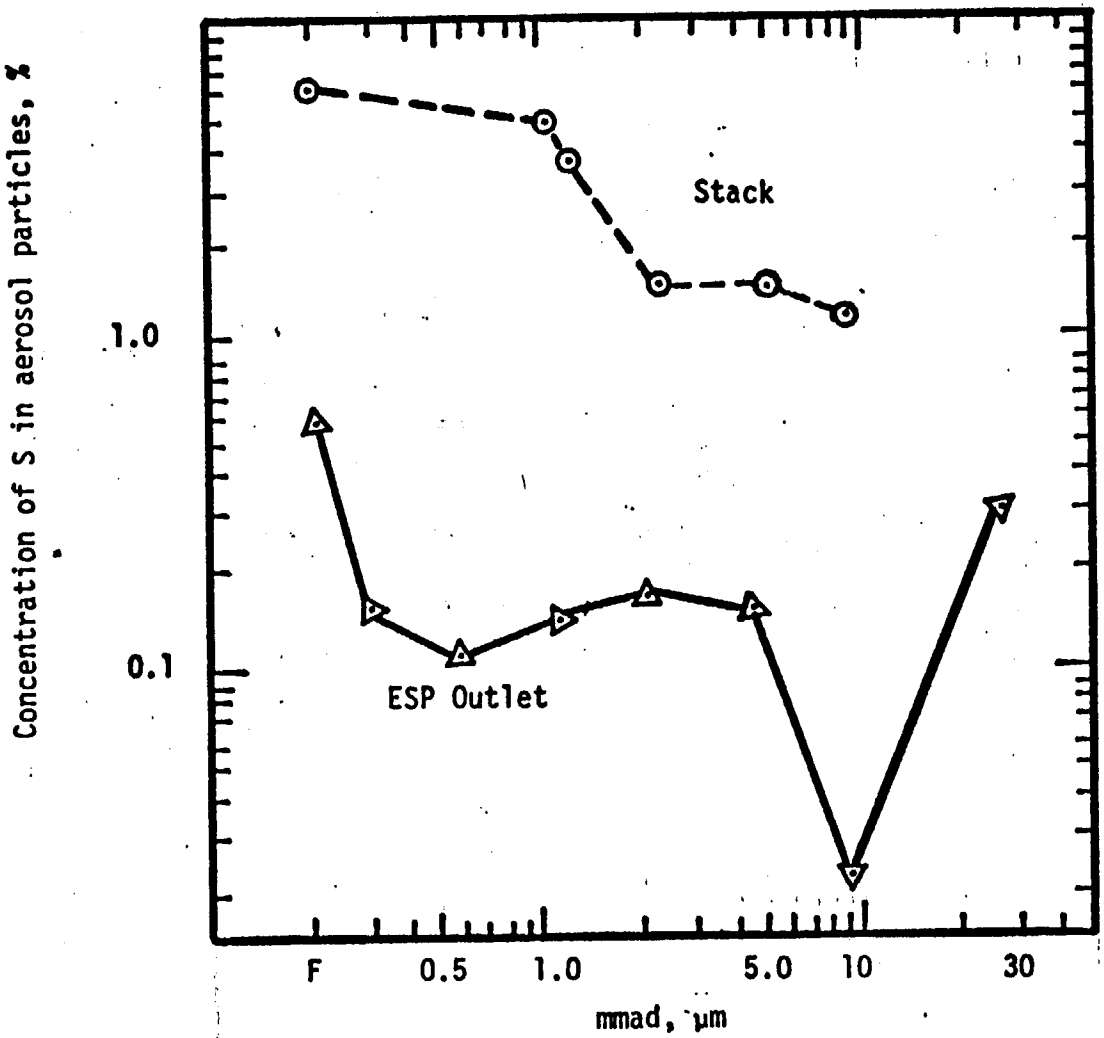


Figure 4b. The relative concentrations of S in aerosol particles are larger in smaller particle sizes.

and concentrated HCl. These properties were used by Andren et al. (Environ. Sci. Technol. 9, 856, 1973) to deduce that Se at an eastern coal-burning steam plant was emitted totally as elemental Se. The volatility and, thus by inference the chemical form of Se during coal combustion is affected by the Ca content of the coal. As noted above, we find less Se in the vapor phase than expected on the basis of the Se content in coal and the volatility of elemental Se. Knowledge of the chemical forms of Se in the fly ash will aid in our understanding of the fate of Se and the effects on Se emission of various control strategies.

A pilot experiment was initiated on fly ash recently collected from the Hunter Plant. Three 1-g aliquots of hopper fly ash were successively extracted with water, 16 M HCl, and 18 M H_2SO_4. Aliquots of the fly ash before and after each extraction are being analyzed for Se by INAA. Each of the extracts were filtered with 0.2-μm Nuclepore filters or centrifuged at speeds of 42,000 rpm for 60 min. to remove fly-ash particles that may contain high concentrations of Se. The particle-free extracts were then transferred to quartz containers and are being activated for Se analyses.

To test the method, four 1-g fly-ash aliquots were doped with 1 mg of either Se powder, SeO_2, Na_2SeO_4, or Na_2SeO_3. Each of the fly-ash aliquots was successively extracted with H_2O, 16 M HCl, and 18 M H_2SO_4.

2. Surface-area studies. Carbonaceous particles often have extremely large specific surface areas and are therefore important gas adsorbants. Activated charcoal, for example, may have specific surface areas on the order of hundreds of m^2/g. Nominal values for size-fractionated fly-ash particles from conventional coal combustion are on the order of 3 or 4 m^2/g. Coal fly ash contains variable quantities of carbon, ranging from a few tenths of a percent to several percent. We are determining the contribution of carbonaceous and other porous constituents of fly ash to the total surface area and their effect on the gas particle partitioning of trace chemical species.

Eight separate 2-lb. hopper-fly-ash samples were collected concurrently with four size-segregated samples of stack fly ash during our February 1976 field trip to the Four Corners Power Plant. A representative portion of each sample was combined to form a single, composite fly-ash sample. The composite sample was then sieved into fractions of >210, 175-210, 125-175, 90-125, 40-90, 20-45, and 20 μm. Surface area (by N_2 adsorption) and carbon content were determined for a sample of each of the sieved fractions and a sample of each of the four stack fly-ash fractions. Both surface area [by the Brunauer, Emmett, and Teller (BET) equation] and a pore volume distribution were calculated for each fraction. The results along with the diameter of average mass are given in Table 6. The mass diameter is the midpoint diameter in the case of the sieved fractions

Table 6. Surface areas and carbon analysis of size fractions.

Sample	Surface area (m^2/g)	Carbon Content (%)	Average mass Diameter (μm)	Dvs (μm)	Pore volume (cc/g)
Cut #4	3.256	0.24	2.5	0.8	.004856
Cut #3	1.722	0.21	3.8	1.5	.00192
Cut #2	0.631	0.22	5.8	4.3	.00085
Cut #1	0.607	0.19	18.5	5.3	.00077
-45 μ	1.05	0.15	32.0	2.86	.0022
45-90 μ	0.863	0.17	65.0	3.48	.0017
90-125 μ	1.293	0.29	110.0	2.32	.0019
125-175 μ	1.306	0.44	150.0	2.30	.0022
175-210 μ	2.567	0.73	190.0	1.17	.0043
+210 μ	4.436	2.67	350.0	0.68	.0010
COMPOSITE (-45, +210)	1.343	0.44	75.0	2.23	.0044

and the mass median diameter in the four stack fly-ash fractions (labeled Cuts 1 through 4). The diameter $D_v s$ is the expected size of the particles based on the surface area, using the following equation for nonporous spherical particles:

$$S = 6/\rho\, d,$$

where ρ is the particle density and d is the particle diameter. In general, these diameters are much smaller than those actually measured. Therefore, the proportion of porous components must be significant.

In Figure 5, surface area is plotted vs. particle size for each of the fly-ash fractions. For particles less than 6 μm in diameter, the slope of the solid curve connecting the data points is consistant with the relationship $S = 6/\rho\, d$ (shown by the dashed curve). This indicates that the surface area can be attributed to the surface of the particles and not to interior portions. This is consistent with our observation that the particles in this size range are predominantly glassy spheres. At larger sizes, the curve passes through a minimum and then increases to a value of about 4.4 m^2/g for the largest sieved fraction. From Table 4 it is evident that the surface area correlates well with the carbon content of the fractions.

The surface areas of particles in the >210 μm fraction and of the composite sample were again determined after the carbon content was analyzed - i.e., after the carbon was removed. The recalculated surface areas were 0.466 and 0.488 m^2/g, respectively. This leads to surface areas of the carbon in the fly-ash particles of 199 and 148 m^2/g. An average of these values (~175 m^2/g) was used as the surface area of the carbonaceous portions of the sieved samples. The net surface areas of the sieved portions without carbon are plotted as open circles in Figure 5. With these points considered, the surface-area dependence on particle size more readily fits the surface area model for porous particles

$$S = \left[\frac{6 - \pi k^2}{\rho\, d} + \frac{2\,\pi k^2}{\rho\, r}\right](1 - \pi k^2),$$

where r = the pore diameter and πk^2 = the fractional pore volume. The value of k that agrees most closely with the pore-volume data is k = 0.05. This value corresponds to a pore volume of about 0.8% and a pore radius of about 0.01 μm.

We recognize that the ashing procedure used to remove carbon may have affected the surface of the particles and, hence, the surface area. We are attempting to confirm the surface-area data after carbon removal in samples that have been ashed at low temperature in an O_2 atmosphere in which O_2 is excited by a 100 w(e) RF generator.

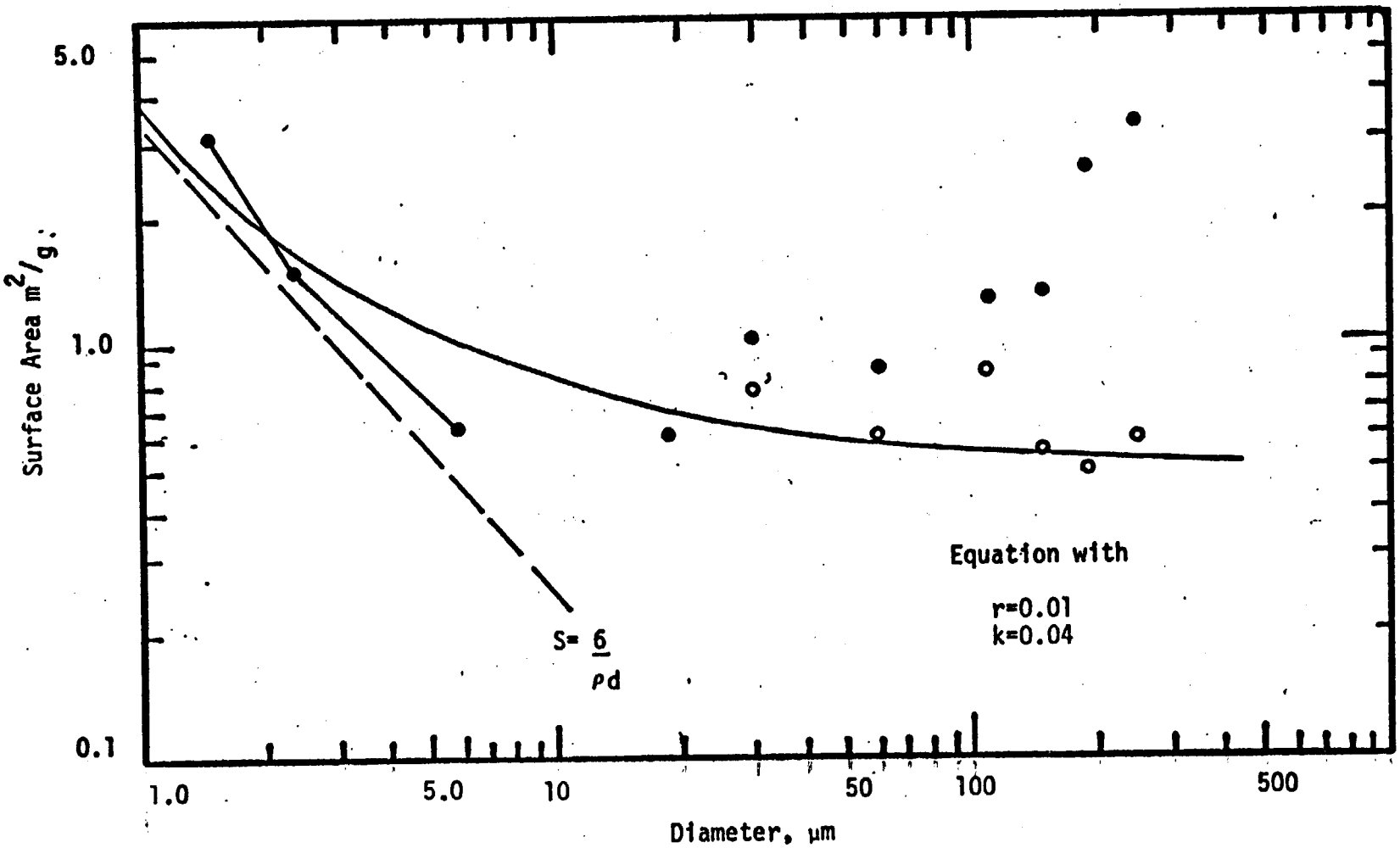


Figure 5. Surface area of fly ash fractions before and after carbon removal (solid and open circles, respectively). The solid curve is the best fit of the data to a porous particle model.

APPENDIX

Table A-1. Filter efficiency experiments, San Juan Power Plant, March, 1979.

Experiment	Filters	Mass (mg)	Volume (m^3)[a]	Concentration (mg/m^3)[a]	Percent of Total
1	Glass fiber -1	16±1	0.451	35.5 ± 2.2	100
	Glass fiber -2	0±1	0.451	<2.2	<6.2
2	Quartz -1	157	0.241	651	99.3
	Glass fiber -3	1.1	0.241	4.5	0.7
3	Teflon -1	13.5	0.117	115.4	100
	Glass fiber -4	0±0.5	0.117	< 4.3	<3.7
4	Teflon -2	0.3	0.056	5.4	100
	Glass fiber -5	0±0.5	0.056	<8.9	< 165
5	Teflon/nylon	ND[b]	2.4	ND	ND
	Quartz -3	1.3	2.4	0.54	ND

[a] gas volume at 70° F and 1 atm.

[b] not determined

TABLE A-2. Aerosol-Particle-Collection Data, San Juan Power Plant, March, 1979.

Date	Experiment	Sample ID	Time of day	Stack Temp, ^{o}F	Volume at 70°F 1 atm, M^3	Sample time (min.)	Isokinecity %	Mass Loading (mg/m^3)	Comment
3/5/79	1	GF1	13:05	350^{o}	0.451	7.5	121	35.5	•47mm glass fiber filter for mass loading
		GF2	13:05	350^{o}	0.451	7.5	121	0.0	•Back-up glass fiber for efficiency check
	2	Q-1	14:00	150-350	0.241	6.0	80	651	•47mm Pallflex quartz
		GF-3	14:00	150-350	0.241	6.0	80	4.5	filter, glass fiber in same holder. Test efficiency of quartz filter. Boiler shut off during test
	3	M-1	14:35	150	0.117	6.0	39	115.4	•47-mm Mitex filter in front holder.
		GF4	14:35	150	0.117	6.0	39	0.0	•47mm Glass fiber filter in separate rear holder. Filter plugged immediately.
3/6/79	4	M-2	08:45	283	0.056	6.0	18	5.4	•Same as experiment 3. Boiler back in operation. Clogged even though little material collected.
	5	MKV-1	09:40	283	0.80	52	77		•Low pressure MKV-
		Q-2 (run1)			0.80				47 -mm quartz filter, Q-2, back-up filter.
	6	MKIII-1 (run 2)	11:08	275	1.04	41	133		•Coated MKIII impactor w/prefilter
		Prefilter GF6			1.04				to test for Se
		Backup GF7			1.04				adsorp. on substrates Prefilter 47-mm glass fiber. Back-up filter 47 mm internal glassfiber

Table A-2 (con't).

DATE	EXPERIMENT #	SAMPLE ID	TIME OF DAY	STACK TEMP, °F	Volume @70°F, 1 atm, M^3	SAMPLE TIME, MIN.	ISOKINECITY	MASS LOADING (mg/m^3)	COMMENT
3/6/79	7	MKV-2 (RUN # 3) GF 8	12:40	275	0.184	10	97	Not Weighed	• Sample for Scanning Electron Microscopy
	8	FP1	13:30	280	2.40	45	107	Not Determined	• 62 mm fluoropore filter 47mm Quartz filter (pallflex) for efficiency test
		Q3	13:30	280	2.40	45	107	0.54	
	9	Q4	-	-	-	-	-	-	• Blank - placed in holder and removed no sample
	10	M3	-	-	-	-	-	-	• Blank - not placed in holder
	11	M4	-	-	-	-	-	-	• Blank - not placed in holder
	12	MKV-3 (Run 5)	-	-	-	-	-	-	• Blank impactor set (uncoated?)

Table A-3. Vapor-Collection Data, San Juan Power Plant, March 1979.

Date	Experiment	Sample ID	Time of Day	STACK TEMP ^{o}F	DILUTION RATIO (DILUTION : SAMPLE)	NET SAMPLE Volume, M^3 @1 atm, 70^{o}F	COMMENT
3/5	1	Char-1	12:25	~365	1.05	0.162	Unit up?
	2	2	14:00	150	0.3	0.130	Unit down
3/6	3	3	08:55	283	0.09	0.258	Unit up
	4	Org 1	10:45	300	1.1	0.251	Unit up
	5	2	12:47	300	1.0	0.117	Unit up
	6	3	13:50	275	2.5	0.148	Unit up

Table A-4, Aerosol-Particle-Collection Data, Huntington Power Plant, July 1979.

Date	Time of day	Filter type	Isokineticity (%)	Sample volume M^3[a]	Mass conc. (mg/m^3)	Comment
7/26	10:28-10:43	LFP 2	63	0.295	225	
	13:02-14:02	MKV-1 LPI	97	0.470	2185	Run with 47mm Fluoropore Filter #3. Pressure at tap 415 mm Hg; Pressure in duct 575 mm Hg.
	15:50-15:60	LFP 9	90	0.250	389	
	16:45-17:15	MKV-2 LPI + Cyclone	81	0.298	1184	Run with 47 mm Fluoropore Filter. Pressure at tap 280-315 mm Hg; Pressure in duct 575 mm. Mass loading doesn't include the cyclone.

[a] at 70°F and 1 atm., dry gas volume.

Table A-5. Filter-Sampling Data, Hunter Power Plant, July and August 1979. ESP-Outlet Location.

Date	Time of day	Sample type	Isokineticity %	Sample volume[a] (m^3)	Mass conc, mg/m^3	Stack temperature (^oF)	Total mass (mg)	% Water	Comments
7/28	15:47-16:45	LFP25	91	1.136	62.7	260	71.3	-	0.104 of filter submitted for SEM/ESCA. 0.896 submitted for INAA.
7/29	10:17-11:52	LFP26	97	2.395	41.0	250	98.2	7.4	
	12:42-14:42	LFP37	100	2.302	26.8	230	61.7	7.7	
	15:14-17:14	LFP33	97	2.719	23.8	255	61.7	-	0.101 submitted for SEM. 0.899 submitted for INAA.
7/30	14:50-16:20	LFP34	103	3.279	(5.84)	245	19.1	6.4	Weight looks too low. Unit down at 08:30. Run for INAA only.
	16:50-17:50	LNF51	106	1.798	-	245	0.552	-	
7/31	08:28-08:45	LPF63	95	0.906	23.4	264	21.2	-	
	12:15-13:17	LFP57	95	1.832	16.7	250	30.5	6.0	
	13:40-14:38	LNF55	88	2.050	15.7	267	32.1	6.0	0.085 submitted for SEM; 0.242 submitted for IC. 0.672 submitted for INAA.
	16:53-19:23	LFP64	99	4.167	15.3	265	63.9	-	0.322 submitted for IC. 0.678 submitted for INAA.
8/1	12:41-14:26	LPF66	103	3.147	(1.4)	275	4.30	-	Power loss during sampling for 16 min. Filter torn, mass too low.
	14:47-15:26	LNF56	98	1.29-1.42	9.7-10.7	277	13.8	-	0.100 submitted for SEM; 0.900 submitted for INAA.
8/2	11:08-12:02	LPF67	99	1.879	17.2	267	32.3	-	
	13:20-14:44	LPF74	111	2.017	18.1	265	36.6	-	
	~15:00-15:02	LNF61	~71	0.076	(27.7)	~265	2.10	-	Weight unreliable due to small sample size. Submitted for SEM only.

Table A-6. Filter-Sampling Data, Hunter Power Plant, July and August 1979. Stack Location.

Date	Time of day	Sample type	Isokineticity (%)	Sample volume[a] (m^3)	Mass conc. (mg/m^3)	Stack temp. (^oF)	Total mass (mg)	% Water	Comment
7/28	12:29-13:51	LFP21[a]	79	3.296	15.1	130	49.67	-	
	15:10-16:46	LFP11	93	3.587	13.7	130	49.13	-	0.118 submitted for SEM/ESCA 0.882 submitted for INAA.
7/29	14:45-15:01	LFP23	91	0.767	10.3	142	7.89	-	
	15:38-16:05	LFP24	94	0.792	8.83	142	7.00	-	
	16:55-17:46	LNF 42[b]	102	0.843	9.82	142	8.28	-	0.088 submitted for SEM/ESCA; 0.912 submitted for INAA.
7/30	14:25-15:15	LNF43	99	1.576	34.6	143	54.5	11.3	Unit outage @ 08:30 ESPs not operating at Peak Efficiency. INAA only.
	17:16-17:52	LFP50	96	1.628	25.3	145	41.21	12.4	
7/31	12:33-14:22	LPF 58[c]	97	6.563	11.1	141	72.78	-	
	16:50-17:52	LFP35	90	2.982	11.3	141	33.63	-	0 .266 IC; 0.734 for INAA.
	18:30-20:02	LNF49	105	2.711	12.3	142	33.43	-	0.100 submitted for SEM/ESCA; 0.672 for INAA; 0.228 for IC.
8/1	10:20-11:20	LPF65	99	3.162	10.5	142	33.20	11.8	
	11:30-13:00	LNF60	98	2.757	10.0	142	27.62	-	0.113 submitted for SEM/ESCA; 0.887 for INAA.
8/2	11:40-11:46	LNF72	1.03	0.0654	-	141	-	-	SEM sample only.

[a]LFP=62MM Fluoropore filter. [b]LNF=62MM Nuclepore filter. [c]LPF=62MM Pallflex filter.

[c]fraction of the gas by-passing the scrubber system.

Table A-7. Impactor-Sampling Data, Hunter Power Plant, July and August 1979. ESP Outlet Location

Date	Time of day	Sample type	Isokinetic ratio (%)	Sample volume (m^3)	Mass conc. (mg/m^3)	Stack temp. (^oF)	Total mass (mg)	Water vapor (%)	Comments
7/30	12:37-14:31	MK3-2	99	2.194	-	235	-	-	LFP#38 used as back-up filter. Stack velocity increased 30% during collection coated impactor.
	18:13-20:44	MK3-4	101	3.392	(5.4)	245	18.3	4.9	LNF53, Run with stages uncoated. Mass Low probably due to a wall loss.
7/31	09:20-11:10	MK3-5	102	2.636	(8.5)	265	22.5	-	LNF54. Run with coated stages. Mass unreliable due to possible coating loss.
	18:44-20:07	MK3-7	95	1.993	-	265	-	-	

Table A-8. Impactor-Sampling Data, Hunter Power Plant, July and August 1979. Stack Location

Date	Time of day	Sample type	Isokineticity	Sample volume (m^3) [a]	Mass Conc. (mg/m^3)	Stack Temp. (^oF)	Total Mass (mg)	% Water	Comments
7/29	10:53-13:26	MK3-1	99%	2.565	-	140	-	-	Run with LFP # 22.
7/30	15:38-16:31	MK5-3	95	0.476	-	146	-	-	Stack pressure, 616 mm Hg; Pressure at tap, 16.5 - 17.3 in Hg. Run with 47 mm fluoropore filter in separate holder.
	19:30-20:05	MK3-3	97	0.746	-	145	-	12.4	Stages run without coating. 62mm Nuclepore filter #52 in separate holder as backup.
7/31	14:38-16:38	MK3-6	102	2.318	(8.3)	141	19.3	12.0	Run with LFP#36 in separate holder. Mass loading probably in error due to loss of coating.
8/2	09:23-11:27	MK3-8	100	2.367	(5.5)	141	13.0	12.6	coated impactor stages.

Table A-9. Inorganic Vapor-Collection Data, Hunter Power Plant, July and August 1979.

Date	Sample ID	Location	Time of day	Flue gas Temperature (°F)	Dilution volume[a] (m^3)	Sample volume[a] (m^3)	Comment
7/29	CHAR 001	Stack	13:36-13:53 14:51-17:50	142	0.987	0.470	47mm,FP39
7/30	CHAR 003	Stack	0:857-09:32	220	0.158	0.141	unit down @08:30
			14:00-17:00	146	0.812	0.796	47mm,FP40
				total	0.970	0.937	
7/30	CHAR 008	Stack	18:00-21:00	145	1.05	0.507	47mm, FP4
8/01	CHAR 010	ESP-outlet	10:35-13:45	275	0.361	0.310	62mm, FP7 pump stopp during sample
8/01	CHAR 005	ESP-outlet	14:05-17:15	275	0.527	0.559	62mm, FP7

[a] Volume at 70°F and 1 atmosphere.

Table A-10. Organic Vapor-Collection Data Hunter Power Plant, July and August, 1979.

Date	Sample ID	Location	Time of day	Flue-gas temp. (°F)	Dilution volume (m^3)[a]	Sample Volume (m^3)[a]	Comment
07/31	HC002	Stack	09:45 - 14:45	141	6.29	1.72	Pallflex # 30 47mm
07/31	HC003	Stack	15:47 - 20:45	141	4.23	3.57	Pallflex # 31 47 mm
08/02	HC001	ESP Outlet	09:16 - 15:46	265	3.51	4.81	Fluoropore #62 mm Trap plugged with ice

[a] at 70°F, 1 atm.

Table A-11. Bulk Samples Collected at the Huntington and Hunter Power Plants July and August, 1979.

Sample Type	Plant	Date	Time of day
Fly Ash	Huntington	7/26	11:30, 17:00
	Hunter	7/28	14:30
		7/29	10:30
		7/30	08:00, 17:00
		7/31	09:10, 15:25
		8/01	11:15
Coal	Huntington	7/25	16:40
		7/26	10:05, 16:32
	Hunter	7/28	13:50
		7/29	14:00
		7/30	08:30, 18:15
		7/31	09:15, 15:35
		8/01	10:10
Thickener Underflow	Hunter	7/30	15:00
		7/31	10:40, 17:50
		8/02	18:00
Scrubber Slurry	Hunter	7/30	15:35
		7/31	11:00, 18:10
		8/02	18:20
Thickener Overflow	Hunter	7/30	16:00
		7/31	10:55, 18:05
		8/02	18:15
Ash water	Hunter	7/30	16:10
		7/31	10:45, 17:55
		8/02	18:05
Lime Slurry	Hunter	7/30	16:15
		7/31	10:50, 18:00
		8/02	18:10

Distribution:

INTERNAL

A. H. Biermann	L-369
E. M. Morimoto/R. C. Ragaini	L-453
W. L. Robison	L-453
J. H. Shinn	L-524
Bio-Med Dept. (25 cys.)	L-452

EXTERNAL

D. S. Ballantine
Office of Health and Environmental Research
Germantown, MD